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Determination of oxygen and sulfur thermodynamic activity in molten metals

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Abstract. The paper describes computer analysis of concentration dependence of oxygen activity coefficients f_o in binary liquid titanium-base alloys containing ions of copper, nickel, molybdenum, vanadium, zirconium and aluminum. The study covers calculations of oxygen activity coefficient f_o and sulphur activity coefficient f_s in binary melts of the systems Cu – Fe, Cu – Ni, Cu – Co, Ni – Co, Fe – Ni, Fe – Co as a function of the concentration of metal components.

The two main equations suggested in [1] and [2] are chosen for calculations. The first one comprises a selectable energy parameter h which is proportional to the enthalpy change in case of interstitial metalloid atom X in tetra– and octahedral vacancies formed by metal atoms:

$$\ln f_{X[A+B]} = ½ \ln [f_{X[A]} f_{X[B]}] - \ln \{\Sigma \binom{z}{i} [(1-N_B) / \Phi^{(1/2)Z}]^{(z-i)} \times \times [N_B \Phi^{(1/2)Z}]^{i} \exp [(((z-i)\, i) / (2RT))h]\}. \quad (1)$$

The second equation involves two parameters h_1 and h_2; h_1 is proportional to the enthalpy change when dissolving atom X in pure solvent A, h_2 is proportional to the difference of enthalpies of X dissolution reactions in pure liquid metal components A and B of the alloy:

$$\ln f_{X[A+B]} = ½ \ln [f_{X[A]} f_{X[B]}] - \ln \{\Sigma \binom{z}{i} [(1-N_B) / \Phi^{(1/2)Z}]^{(z-i)} \times \times [N_B \Phi^{(1/2)Z}]^{i} \exp [((z-i)\, i\, (h_1 - h_2)) / (2RT) + ((z^2 - i^2)\, i\, h_2) / (6RT)]\}. \quad (2)$$

In these equations, $f_{X[A]}$, $f_{X[B]}$, $f_{X[A+B]}$ are the activity coefficients of metalloid X in pure liquid metals A, B and their binary mixture, respectively; N_B is the mole fraction of component B; z is the coordinate number; i is the number of metal atoms A and B surrounding interstitial atom of metalloid X which varies within 0 to z. Coefficient $\Phi = f_{X[A]} / f_{X[B]}$; parameter h varies within $h/2RT < 1/5 \ln \Phi$ [1].

The values f_o in pure molten metals required for calculations are taken from [3-5]; the values f_s in the same liquid metals are taken from [6-10].

When evaluating h, the respective partial molar enthalpies presented in [11,12] are used for calculations of changes in enthalpies between successive steps of reaction of metalloid atom dissolution in molten metals.

The calculation results are given in Table 1 and Table 2.

Table 1. Coefficients of Oxygen Activity in Titanium-Base Melts at 2000 K

System		-Ln f_O Eq. 1	-Ln f_O Eq. 2	System		-Ln f_O Eq. 1	-Ln f_O Eq. 2
Ti - Cu				Ti - Zr			
0.8	0.2	0.3	0.8	0.8	0.2	2.6	2.9
0.6	0.4	0.6	1.4	0.6	0.4	4.6	4.8
0.4	0.6	2.0	2.7	0.4	0.6	6.5	6.6
0.2	0.8	3.5	4.0	0.2	0.8	7.6	7.7
Ti - Ni				Ti - V			
0.8	0.2	0.4	0.3	0.8	0.2	3.0	3.2
0.6	0.4	0.1	1.0	0.6	0.4	5.5	5.5
0.4	0.6	1.0	1.9	0.4	0.6	6.9	7.0
0.2	0.8	3.2	3.6	0.2	0.8	8.5	8.7
Ti - Mo				Ti - Al			
0.8	0.2	0.5	0.9	0.8	0.2	7.3	7.5
0.6	0.4	1.0	1.8	0.6	0.4	10.5	11.0
0.4	0.6	2.2	3.2	0.4	0.6	13.0	13.2
0.2	0.8	3.8	4.9	0.2	0.8	14.0	14.3

It is determined that as the concentration of the second metal component in the melt Ti – Me is increasing, the oxygen activity coefficient is decreasing, at that f_o is mostly reduced in the systems titanium – zirconium, titanium – vanadium, titanium – aluminum. This can be caused by a significant difference between energies of interparticle interactions E_{ij} in melts. The oxygen activity coefficients in binary titanium-base melts can be arranged in a row $f_o^{Al} < f_o^{V} < f_o^{Zr}$; $f_o^{Mo} < f_o^{Ni} < f_o^{Cu}$. This sequence qualitatively correlates with the values characterizing the change in standard Gibbs energies ΔG^O of oxides formation of the respective elements [12].

Table 2. Concentration Dependence of Oxygen and Sulphur Activity Coefficients in Metal Copper-, Iron- and Nickel-Base Melts at 1873 K.

System		-Ln f_O			-Ln f_S		
N_A	N_B	Eq. 1	Eq. 2	Eq. 5	Eq. 1	Eq. 2	Eq. 5
Cu - Fe							
0.8	0.2	3.82	3.35	3.61	3.11	3.27	3.55
0.6	0.4	4.60	4.25	4.00	4.25	4.03	3.84
0.4	0.6	4.88	4.52	4.45	4.63	4.15	3.96
0.2	0.8	4.95	4.55	4.54	4.78	4.27	4.18
Cu - Ni							
0.8	0.2	1.36	1.24	0.95	0.92	1.09	0.77
0.6	0.4	1.60	1.51	1.35	1.02	1.16	0.94
0.4	0.6	1.66	1.58	1.46	1.23	1.22	1.11
0.2	0.8	1.55	1.52	1.49	1.35	1.3	1.17
Cu - Co							
0.8	0.2	2.10	1.85	1.39	1.74	1.60	1.09
0.6	0.4	2.51	2.44	2.07	2.12	2.09	1.55
0.4	0.6	2.40	2.66	2.38	2.18	2.28	1.82
0.2	0.8	2.27	2.62	2.49	2.20	2.18	1.90
Ni - Co							
0.8	0.2	1.20	1.24	1.28	1.00	1.05	1.08
0.6	0.4	1.43	1.44	1.48	1.15	1.15	1.17
0.4	0.6	1.59	1.63	1.66	1.23	1.26	1.35
0.2	0.8	1.72	1.68	1.78	1.45	1.48	1.50
Fe - Ni							
0.8	0.2	4.49	4.18	4.52	4.04	4.16	4.05
0.6	0.4	4.14	3.78	4.17	3.62	3.65	3.88
0.4	0.6	3.52	3.31	3.61	3.00	3.03	3.50
0.2	0.8	2.30	2.46	3.00	2.22	2.16	2.98
Fe - Co							
0.8	0.2	4.25	4.21	4.26	3.93	4.00	3.75
0.6	0.4	3.84	3.75	3.95	3.44	3.56	3.43
0.4	0.6	3.28	3.19	3.40	2.98	2.94	3.22
0.2	0.8	2.56	2.45	2.67	2.20	2.32	2.40

Analysis of f_X given in Table 1 and Table 2 shows that both the models produce the correlating results in the range of low, or to the contrary, rather high concentrations N_B of the second component in the metal compound. Under these conditions, the system is no longer a ternary system, therefore

consideration of the second energy parameter becomes insignificant. At mean concentrations, the values f_X calculated according to equation (2) are a little more for all the systems except for the nickel-cobalt system melts. The values f_S (Table 2) are more than f_o which is not in conflict with the assumptions of oxygen behavior in the melt as an element having higher electronegativity and less sizes compared to those of sulphur ions S^{2-}.

Additions of iron, nickel and cobalt to molten copper result in decreasing of f_o. The growth of iron concentration in the melt has the strongest influence on f_o. This phenomenon can be caused by local areas of prevailing arrangement of iron atoms around oxygen atoms due to their high chemical affinity. Upon achieving the nickel or cobalt concentration $N_i \geq 0.6$, the increase in f_o in liquid copper can be connected with formation of unmixed areas in the melts of copper-nickel, copper-cobalt systems containing the higher concentrations of the second component. Cobalt addition to molten nickel results in decreased f_o. Increase in f_o with the growth of nickel or cobalt concentration in the melts of iron-nickel, iron-cobalt systems is apparently caused by release of a certain portion of oxygen when iron atoms in the melt are replaced with other atoms of less energy of binding with oxygen.

The results show that f_X calculated according to equation (2) closely resemble the literature data [2,3,13]. Equation (1) correctly describes the general behavior of f_X as a function of composition. Considering of two parameters is effective if there is a significant difference between heats $\Delta H_{[i]}$ of metalloid dissolution in pure metals. In case of near values $\Delta H_{[i]}$ the results of calculation according to equations (1), (2) do not differ much.

In spite of diversity of analytical equations, all the existing model have thermodynamic concepts based on the assumptions of random distribution of atoms in liquid metal compounds and do not consider the system entropy change, which always occurs during dissolving. Moreover, activity calculations according to equations (1), (2) are accompanied by some difficulties relating to determination of parameters h, h_1, h_2 which are introduced into the equations for the heuristic purpose.

The study includes the trial to determine the analytical equation which would contain the parameters characterizing nonadditivity of binding energy of different pairs of atoms in the melt and their arrangement ordered to a certain extent at the temperatures which do not too exceed the alloy melting point. These parameters are ΔH and ΔS, i.e. change in enthalpy and entropy of metal compound when dissolving metalloid atoms in the melt.

The main formulas are derived based on the known equation [14]:

$$\mu_i - \mu_i^{st} = RT \ln a_i , \quad (3)$$

where μ_i is the chemical potential of the component in the actual solution; μ_i^{st} is the chemical potential of the component in the standard state.

The difference between chemical potentials of the component in the solution is governed by the change in partial molar quantity of Gibbs energy during dissolving. The latter is the difference between the partial molar quantities characterizing the change in the component dissolution enthalpy and entropy at T = const:

$$\mu_i - \mu_i^{st} = \bar{G}_i - G_i^{st} = \Delta\bar{G}_i = \Delta\bar{H}_i - T\,\Delta\bar{S}_i , \quad (4)$$

where $\Delta H_i = \bar{H}_i - \bar{H}_i^0$, $\Delta S_i = \bar{S}_i - \bar{S}_i^0$, and $\bar{H}_i$ and $\bar{S}_i$ are partial molar enthalpy and entropy in the solution, H_i^0 and S_i^0 are the respective values of these parameters for the pure component.

The equation describing the concentration dependence of the metalloid activity coefficients for its dilute solutions in binary liquid metal systems is as follows:

$$\ln f_{X[A+B]} = \ln [f_{X[A]} f_{X[B]}] + \ln [P \exp(\Delta H_{mix}/(RT) \exp(-\Delta S_{mix}/R)]. \quad (5)$$

In equation (5) the first term characterizes the interdependent contribution of metal atoms into near ordering in the melt; P is the multiplier that determines the mixing heat portion depending on the contribution of the neighbors' interaction energy, and is calculated according to [15] using the data on surface tension and change in the component volumes during mixing, the latter are classified in [16,17].

The values ΔH_{mix} are calculated according to the equation

$$\Delta H_{mix} = (\Delta H_{O[A]} + \Delta H_{O[B]}) - \Delta H_{O[A+B]}. \quad (6)$$

where $\Delta H_{O[A]}$ and $\Delta H_{O[B]}$ are thermal effects typical of reactions of metalloid dissolution in liquid pure metals A and B; $\Delta H_{[A+B]}$ is an enthalpy change resulting from formation of binary metal alloy, this value depends on concentration and is taken from [18,19] for the systems under study.

The entropy change of binary metal compound with oxygen as a function of composition is calculated based on the method described in [20] and the data of X-ray structural analysis of liquid metal systems [21]. ΔS_{mix} is presented as the difference between additive entropy of component A and component B when dissolving oxygen therein, and excess entropy of metal atom mixing during binary alloy formation:

$$\Delta S_{mix} = (S_{O[A]} + S_{O[B]}) - \Delta S_{[A+B]} . \quad (7)$$

The results of calculation for f_o and f_s according to equation (5) and given in Table2 have the same order as f_o and f_s determined according to equations (1), (2) and resemble the experimental data [11,12].

REFERENCES

[1] Wagner C. // Acta Met. 1973. 21 № 9. P. 1297 – 1303.
[2] Chiang T., Chang Y. The activity coefficient of oxygen in binary liquid metal alloys // Met. Trans.1976.7B.P.453-467.
[3] Kamori Nobumasa, Katayama Iwao. // J. Japan Inst. Metals. 1980. 44. №2. P. 197-201.
[4] Fisher W., Ianke P. // Arch. Eisenhutt. 1971. 42 №10. S. 691-694.
[5] Pekka T. // Scand. J. Met. 1979. 8. №3. P. 123-127.
[6] Fitzner K. // Arch. Hutn. 1980. 25.№2. P. 137-142.
[7] Ishii Fujio, Fuwa Tasuku. // J. Iron and Steel Inst. Japan. 1981. 67. №6. P.746.-754.
[8] A.V. Taberko, S.E. Vaisburd, L.Sh. Tsemekhman. Study of thermodynamics of suphide nickel-sulphur melts at sulphur content up to five atomic percent by vapour pressure measurement. – Lib: Sulphide melts of heavy metals. Moscow: Nauka, 1982. pp.7-11.
[9] Hayashi Shoji, Uno Tatsuji. // J. Iron and Steel Inst. Jap. 1982. 68. №13. P. 1728-1736.
[10] K.V. Grigorovich, V.Ya. Dashevsky.//Magazine Physical Chemistry.1984. 58. №4. C.998-1000.
[11] B.M. Lepinskih. Oxidation of liquid metals and alloys/ B.M. Lepinskih, A.A.Kitashov, A.A.Belousov. Moscow: Nauka, 1979. pp.112.
[12] I.S. Kulikov. Metal Deoxidation. Moscow: Metallurgy, 1975. pp. 340 c.
[13] V.M.Denisov. Structure and properties of molten oxides / V.M.Denisov, N.V.BElousova, S.A.Istomin, S.G.Bakhvalov, E.A.Pastukhov. Ekaterinburg: Ural Branch of the Russian Academy of Sciences, 1999. pp. 498.
[14] A.A.Zhukhovitsky. Physical chemistry / A.A.Zhukhovitsky, L.A. Schwarzman. Moscow: Metallurgy, 2001. pp. 686
[15] O.A. Esin, N.A. Vatolin, V.F. Ukhov. Physical chemistry of metallurgic melts: Tractate.Metal institute. Ural Research Centre of the USSR Academy of Sciences. Sverdlovsk: Metal institute. Ural Research Centre of the USSR Academy of Sciences, 1969. Issue.18. pp.87 – 103
[16] V.I. Nizhenko. Surface tension of liquid metals and alloys / V.I. Nizhenko, L.I. Floka. Moscow: Metallurgy, 1981. pp. 210.
[17] S.I. Popel. Surface phenomena in melts. Moscow: Metallurgy, 1994. pp. 432.
[18] A.M. Samarin, A.A. Vertman. Thermochemistry of iron- and nickel-base melts // Proceedings of the USSR Academy of Sciences.Metals. 1966.No.3. pp.19-30.
[19] G.I. Batalin, V.S. Sudavtsova. Thermodynamic properties of Fe-Cu liquid alloys // Proceedings of the USSR Academy of Sciences. Metals. 1980. No.2. pp. 45-49.
[20] Mansoori G. A., Carnahan N. F., Starling K. E. Thermodynamics properties of the mixture of hard spheres // J. Chem. Phys. 1971. 54. №4. P. 1523-1525.
[21] I.Vaseda. Structure of liquid transition metals and alloys / Lib:Liquid Metals. Moscow: Metallurgy,1980. pp.182-193.